

APPLICATION
FOR
UNITED STATES LETTERS PATENT

TITLE: **THERMAL EXTENDERS FOR WELL FLUID
APPLICATIONS INVOLVING SYNTHETIC
POLYMERS**

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Thermal Extenders for Well Fluid Applications Involving Synthetic Polymers

Cross-Reference to Related Applications

[0001] This Application claims the benefit of U.S. Provisional Patent Application No. 60/297,491, filed on June 11, 2001.

Background of Invention

Field of the Invention

[0002] The invention relates generally to the exploitation of hydrocarbon-containing formations. More specifically, the invention relates to the fields of fluid rheology, thickeners, viscosifiers, viscoelastic fluids, drilling fluids, well fracturing fluids, well treatment fluids and fluid control pills.

Background Art

[0003] When drilling or completing wells in earth formations, various fluids typically are used in the well for a variety of reasons. The fluid often is aqueous. For the purposes herein, such fluid will be referred to as "well fluid." Common uses for well fluids include: lubrication and cooling of drill bit cutting surfaces while drilling generally or drilling-in (*i.e.*, drilling in a targeted petroliferous formation), transportation of "cuttings" (pieces of formation dislodged by the cutting action of the teeth on a drill bit) to the surface, controlling formation pressure to prevent blowouts, maintaining well stability, suspending solids in the well, minimizing fluid loss into and stabilizing the formation through which the well is being drilled, fracturing the formation in the vicinity of the well, displacing the fluid within the well with another fluid, cleaning the well, testing the well,

implacing a packer fluid, abandoning the well or preparing the well for abandonment, and otherwise treating the well or the formation. Brines (such as CaBr_2) commonly are used as well fluids because of their wide density range and the fact that brines are typically substantially free of suspended solids. Additionally, brines typically do not damage certain types of downhole formations.

[0004] A variety of compounds typically are added to the brine-based well fluids. For example, a brine-based well fluid also may include corrosion inhibitors, lubricants, pH control additives, surfactants, solvents, and/or weighting agents, among other additives. Some typical brine-based well fluid viscosifying additives include synthetic polymers and oligomers such as poly(ethylene glycol) (PEG), poly(diallyl amine), poly(acrylamide), poly(aminomethylpropylsulfonate [AMPS]), poly(acrylonitrile), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl amine), poly(vinyl sulfonate), poly(styryl sulfonate), poly(acrylate), poly(methyl acrylate), poly(methacrylate), poly(methyl methacrylate), poly(vinylpyrrolidone), poly(vinyl lactam) and co-, ter-, and quater-polymers of the following comonomers: ethylene, butadiene, isoprene, styrene, divinylbenzene, divinyl amine, 1,4-pentadiene-3-one (divinyl ketone), 1,6-heptadiene-4-one (diallyl ketone), diallyl amine, ethylene glycol, acrylamide, AMPS, acrylonitrile, vinyl acetate, vinyl alcohol, vinyl amine, vinyl sulfonate, styryl sulfonate, acrylate, methyl acrylate, methacrylate, methyl methacrylate, vinylpyrrolidone, and vinyl lactam.

[0005] The synthetic polymers and oligomers listed above have other uses in drilling applications as well. When drilling progresses to the level of penetrating a hydrocarbon bearing formation, special care may be required to maintain the stability of the wellbore. Examples of formations in which problems often arise are highly permeable and/or poorly consolidated formations. In these types of formations, a technique known as "under-reaming" may be employed.

[0006] In this process, the wellbore is drilled to penetrate the hydrocarbon bearing zone using conventional techniques. A casing generally is set in the wellbore to a point just above the hydrocarbon bearing zone. The hydrocarbon bearing zone then may be re-drilled, for example, using an expandable under-reamer that increases the diameter of the wellbore. Under-reaming usually is performed using special "clean" drilling fluids. Typical drilling fluids used in under-reaming are expensive, aqueous, dense brines that are viscosified with a gelling and/or cross-linked polymer to aid in the removal of formation cuttings. The high permeability of the target formation, however, may allow large quantities of the drilling fluid to be lost into the formation.

[0007] Once the drilling fluid is lost into the formation, it becomes difficult to remove. Calcium and zinc-bromide brines can form highly stable, acid insoluble compounds when reacted with the formation or substances contained therein. This reaction may reduce the permeability of the formation to any subsequent out-flow of the targeted hydrocarbons. The most effective way to prevent such damage to the formation is to limit fluid loss into the formation.

[0008] Thus, providing effective fluid loss control is highly desirable to prevent damaging the formation in, for example, completion, drilling, drill-in, displacement, hydraulic fracturing, work-over, packer fluid emplacement or maintenance, well treating, or testing operations. Techniques that have been developed to control fluid loss include the use of fluid loss "pills." Significant research has been directed to determining suitable materials for the fluid loss pills, as well as controlling and improving the properties of the fluid loss pills. Typically, fluid loss pills work by enhancing filter-cake buildup on the face of the formation to inhibit fluid flow into the formation from the wellbore.

[0009] Because of the high temperatures, high shear (caused by the pumping and placement), high pressures, and low pH to which well fluids are exposed (*i.e.*,

“stress conditions”), the synthetic polymeric materials used to form fluid loss pills and to viscosify the well fluids tend to degrade rather quickly. What is needed are synthetic polymer compositions that can withstand the stress conditions for extended periods of time without significant degradation. In particular, what is needed is a simple, inexpensive way to increase the thermal range for viscosifying agents used in downhole applications. Preferably, this thermal extender would be applicable to various viscosifying agents.

Summary of Invention

- [0010] In one aspect, the present invention relates to a method for increasing the thermal and pressure stability of viscosifying agents, particularly synthetic polymers, used in a well fluid which comprises mixing a miscible tertiary amine compound into the fluid.
- [0011] In another aspect, the present invention relates to a method for increasing the thermal and pressure stability of viscosifying agents, and particularly synthetic polymers, in a well fluid which comprises mixing a miscible secondary amine compound into the fluid.
- [0012] In another aspect, the present invention relates to a method for increasing the thermal and pressure stability of viscosifying agents, and particularly synthetic polymers, in a well fluid which comprises mixing a miscible primary amine compound into the fluid.
- [0013] In another aspect, the present invention relates to a thermally stable viscosifying system for well fluids which comprises a synthetic polymer, a solvent, and a tertiary amine miscible in the solvent.
- [0014] In another aspect, the present invention relates to a thermally stable viscosifying system for well fluids, which comprises a synthetic polymer, a solvent, and a secondary amine miscible in the solvent.

[0015] In another aspect, the present invention relates to a thermally stable viscosifying system for well fluids, which comprises a synthetic polymer, a solvent, and a primary amine miscible in the solvent.

[0016] Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

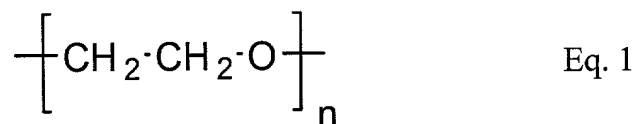
Detailed Description

[0017] The present invention relates to a novel composition for increasing the thermal durability of synthetic polymers used in downhole applications. Further, the present invention relates to increasing the thermal and pressure stability of viscosified well fluids by including an effective amount of an amine into a synthetic polymer system. "Effective" simply means an amount sufficient to raise the temperature stability of the synthetic polymer system by a measurable amount.

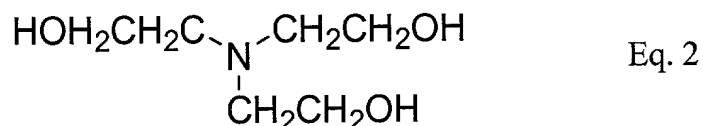
[0018] In general, the present invention relates to compositions for the creation of, and methods of using fluid loss control pills and similar fluids that can sustain stress conditions for extended periods of time without significant fluid loss or loss of desirable rheological properties. The stress conditions may include, for example, exposure to high shear in pumping and placement, exposure to oxidizing breakers (including oxygen dissolved in the fluid), exposure to brines having high divalent cation content, high temperature, high differential pressure, low pH, extended time, and a combination of two or more of such stress conditions. These pills and fluids are advantageously applied in or in connection with drilling, drill-in, displacement, completion, hydraulic fracturing, work-over, packer fluid impacement or maintenance, well treating, testing, or abandonment.

[0019] In general, one embodiment of the invention is related to the effect of triethanol amine (TEA) on a conventional synthetic polymer well fluid system, such as a system containing polyethylene glycol (PEG). PEG is a water soluble

polymer that may be generated from a condensation reaction between ethylene glycol monomers. The general structure of a single repeat unit of PEG is shown below:



[0020] Triethanol amine (TEA) has the following structure:



[0021] In one embodiment, the effects of high temperatures for long periods of time on the fluid control abilities of synthetic polymers were measured on a TEA-containing composition. Specifically, 10.0 grams per lab barrel (g/Lbbl) of high molecular weight PEG (MW ~ 400,000 g/mol) and 7.0 g/Lbbl of low molecular weight PEG (MW ~ 800 g/mol) were added slowly to an agitated brine solution. Note that throughout the specification, the term “lab barrel” is used as a unit of volume - a lab barrel is equivalent to about 350 milliliters. (A lab barrel of water weighs about 350 grams, just as a regular barrel of water weighs the same number of pounds, about 350. This is the formal origin of the term “lab barrel.” Additionally, while the particular embodiments describe a particular order of addition for the chemical components, such a description is not intended to limit the scope of the invention in any fashion.

[0022] In this embodiment, the brine solution comprises 0.888 Lbbl of a 19.2 pounds per gallon (ppg) density ZnBr_2 / CaBr_2 in water. The 19.2 pounds per gallon ZnBr_2 / CaBr_2 brine solution is roughly 52.8% by weight ZnBr_2 , 22.8% CaBr_2 , with the balance being water. Next, 15.0 g/Lbbl amount of an oxygen scavenger (sodium thiosulfate pentahydrate in this embodiment) was mixed as a dry reagent into the brine. Next, 5.0 g/Lbbl of TEA (85 % TEA in water) was

added to the brine. After the addition of the TEA, 5.0 g/Lbbl of gilsonite was added as a dry reagent into the brine. Gilsonite is a natural, resinous hydrocarbon which is often used as an additive in well fluids because of its corrosion inhibiting properties. In addition, 5.0 g/Lbbl of lignite was added to the brine as a dry reagent. To this mixture, 30.0 g/Lbbl of calcium carbonate (CaCO_3) was added. It should be noted that all of the additional chemicals added to the TEA / PEG / brine system discussed above were added only to approximate a "typical" well fluid. It is explicitly within the scope of the invention that a variety of other well fluid additives may be present in addition to the amine/ synthetic polymer / brine system described above.

[0023] The fluid loss properties of the compositions described in the following embodiments were determined as follows. Fluid loss tests of durations ranging from 30 seconds to 48 hours were performed in an API standard high pressure high temperature (HPHT) apparatus (Ref.: API 13-B1 with one modification: substituting an Aloxite or ceramic disk for paper). The testing temperature used in obtaining the below readings was predetermined, such as, for example, in accordance with a bottom-hole temperature at which the fluid will be used in the field. The HPHT apparatus was operated at 250 to 600 psig differential pressure, using, for example, a 50-2000 milliDarcy Aloxite disc (HPHT cell). In general, the HPHT cell is loaded into the HPHT apparatus, which is then pressurized and heated to a predetermined temperature. A discharge valve located on the HPHT apparatus is then opened, and a filtrate volume is measured as a function of time.

[0024] In the first embodiment, after mixing the above components, the composition was placed in a HPHT cell and heated for 45 minutes at 250 °F. In this embodiment, a HPHT cell fitted with an Aloxite disk having a nominal permeability of 60 milliDarcys was used. After allowing the HPHT cell to cool, the HPHT cell was placed into the HPHT apparatus and was pressurized to 500

psig at a temperature of 395° F. The amount of fluid loss was then recorded over approximately 10 to 15 minute intervals for 6 hours. The tables reproduced in the specification, therefore, merely extract the relevant data, rather than reproducing the data *in toto*.

[0025] For comparison, an experiment was run under conditions similar to those described above without the addition of TEA. In the comparison, 15.0 g/Lbbl of high molecular weight PEG (MW ~ 400,000 g/mol) and 7.0 g/Lbbl of low molecular weight PEG (MW ~ 800 g/mol) were added slowly to 0.879 Lbbl of agitated brine solution. As in the previous embodiment, the brine solution comprised a 19.2 pounds per gallon (ppg) ZnBr₂ / CaBr₂ in water. The lignite, gilsonite, calcium carbonate, and oxygen scavenger were added as in the above embodiment. The amounts of lignite, gilsonite, and calcium carbonate were substantially identical to those described above, while less (5.0 g/Lbbl compared to 15.0 g/Lbbl) oxygen scavenger was used.

[0026] As in the first embodiment, after mixing the above components, the composition was placed in a HPHT cell and heated for 45 minutes at 250 °F. In this embodiment, a HPHT cell fitted with an Aloxite disk having a nominal permeability of 60 milliDarcys was used. After allowing the HPHT cell to cool, the HPHT cell was placed into the HPHT apparatus and was pressurized to 500 psig at a temperature of 395° F. The amount of fluid loss was then recorded over approximately 10 to 15 minute intervals for approximately 6 hours.

[0027] The results are summarized below:

Composition	30 sec	15 min	30 min	60 min	90 min	180 min	285 min	350 min
Embodiment 1	2.0	no reading	5.0 (27 min)	no reading	6.8	8.4	10.1	11.5

Composition	30 sec	15 min	30 min	60 min	90 min	180 min	285 min	350 min
Comparative Example	10	25	63	147	blowout (70 min)	-----	-----	-----

TABLE 1: COMPARISON OF FLUID LOSS (MEASURED IN ML) FOR TEA VS. NON-TEA SYSTEMS

[0028] The data in Table 1 shows that the TEA containing system prevents significant fluid loss from occurring, while the system without the TEA suffers a “blowout” (*i.e.*, the loss of all fluid) after 70 minutes. The TEA-containing system, however, maintains its integrity even after approximately 6 hours. Further experiments revealed that the fluid control properties of the TEA-containing system remain substantially intact under the HPHT conditions described above for at least 48 hours. The loss of fluid control exhibited by the non-TEA-containing system is attributed, at least in part, to polymer degradation. A mechanism for how TEA provides the additional thermal stability (as shown in Table 1) is proposed below.

[0029] In a second embodiment, the effectiveness of the TEA on a system having higher PEG concentration than the first embodiment was determined. In this embodiment, 15.0 g/Lbbl of high molecular weight PEG (MW ~ 400,000) and 7.0 g/Lbbl of low molecular weight PEG were added to 0.888 Lbbl of a 19.2 ZnBr₂ / CaCl₂ in water. As in the first embodiment, the 19.2 pounds per gallon ZnBr₂ / CaBr₂ water mixture is roughly 52.8% by weight ZnBr₂, 22.8% CaBr₂, with the balance being water. To the PEG / brine mixture, the oxygen scavenger, lignite, gilsonite, TEA, and calcium carbonate were added in the same amounts and in the same manner as in the first embodiment described above.

[0030] As in the first embodiment, after mixing the above components, the composition was placed in a HPHT cell and heated for 45 minutes at 250 °F. In

the second embodiment, a HPHT cell fitted with an Aloxite disk having a nominal permeability of 60 milliDarcys was used. After allowing the HPHT cell to cool, the HPHT cell was placed into the HPHT apparatus and was pressurized to 500 psig at a temperature of 395° F. The amount of fluid loss was then recorded over approximately 10 to 15 minute intervals for approximately 6 hours.

[0031] The results are summarized below:

Composition	30 sec	6 min	27 min	70 min	90 min	180 min	285 min	350 min
Embodiment 1	2.0	3.8	5.0	5.8	6.8	8.4	10.1	11.5
Embodiment 2	3.2	4.0	5.1	5.6	6.0	7.6	9.5	10.0

**TABLE 2: COMPARISON OF FLUID LOSS (MEASURED IN mL) FOR HIGHER
CONCENTRATION PEG**

[0032] The data in Table 2 shows that the system suffers substantially no adverse effect on the fluid control properties (*i.e.*, the thermal stability) when the concentration of PEG is raised by about 50%.

[0033] In a third embodiment, the effect of increased TEA concentration was determined. In this embodiment, 15.0 g/Lbbl of high molecular weight PEG and 7 g/Lbbl of low molecular weight PEG were added to 0.676 Lbbl of 19.2 ppg ZnBr₂ / CaBr₂ in water. To this mixture, 80.0 g/Lbbl of TEA was added. In addition, the oxygen scavenger, the lignite, the gilsonite, and the calcium carbonate were added in the same amounts and in the same manner as in the first and second embodiments.

[0034] As in the first and second embodiments, after mixing the above components, the composition was placed in a HPHT cell and heated for 45

minutes at 250 °F. In the third embodiment, a HPHT cell fitted with an Aloxite disk having a nominal permeability of 60 milliDarcys was used. After allowing the HPHT cell to cool, the HPHT cell was placed into the HPHT apparatus and was pressurized to 500 psig at a temperature of 395° F. The amount of fluid lost was then recorded over approximately 10 to 15 minute intervals for approximately 3 hours.

[0035] The results are tabulated below:

Composition	30 sec	27 min	70 min	90 min	180 min
Embodiment 3	7.0	16.0 (25 min)	40.0 (75 min)	45.0	101 (190 min)

TABLE 3: FLUID LOSS (MEASURED IN ML) FOR HIGHER CONCENTRATION TEA

The data in Table 3 shows that higher amounts of TEA still prevent a blowout from occurring.

[0036] In a fourth embodiment, the effect of TEA on mixed polymer systems was determined. In this embodiment, 15.0 g/Lbbl of high molecular weight PEG and 7.0 g/Lbbl of low molecular weight PEG were added to 0.648 Lbbl of 19.2 ZnBr₂ / CaBr₂ in water. Then, 3.0 g/Lbbl of a polymer sold under the trade name HE-300 and 3.0 g/Lbbl of a polymer sold under the trade name of HE-400 were added. Both HE-300 and HE-400 are sold by Drilling Specialties, Inc. of Bartlesville, OK 74004. HE-300 and HE-400 polymers are a family of synthetic, divalent-cation-tolerant, high temperature polymers that work in brine and freshwater environments for many applications. In addition, they may be crosslinked, so that they form rigid gels in a petroleum bearing reservoir for conformance control of unwanted water or gas production. When drilling or completing with clear brine fluids, HE-300 and HE-400 polymers have been used to viscosify brines at temperatures as high as 240°C and will remain stable in solution without

precipitation. 87.0 g/Lbbl of TEA was then added to this mixture. 5.0 g/Lbbl of both lignite and gilsonite were then added to the mixture. In addition, 10.0 g/Lbbl of magnesium oxide and 30.0 g/Lbbl of calcium carbonate were added as dry reagents.

[0037] As in the above embodiments, after mixing the above components, the composition was placed in a HPHT cell and heated for 45 minutes at 250 °F. In the fourth embodiment, a HPHT cell fitted with an Aloxite disk having a nominal permeability of 60 milliDarcys was used. After allowing the HPHT cell to cool, the HPHT cell was placed in the HPHT apparatus and was pressurized to 500 psig at a temperature of 395° F. The amount of fluid loss was then recorded over approximately 10 to 15 minute intervals for approximately 16 hours.

[0038] The results are summarized below:

Composition	30 sec	20 min	60 min	120 min	215 min	375 min	965 min
Embodiment 4	6.0	7.0	8.0	15.0	22.0	49.0	94.0

TABLE 4: FLUID LOSS (MEASURED IN mL) FOR TEA/ MIXED POLYMER SYSTEMS

[0039] The data in Table 4 shows that even when subjected to temperatures well in excess of 250 °F, the TEA /mixed polymer system maintains its thermal / pressure stability.

[0040] In addition, while specific amounts of the chemicals used are described in the above embodiments, it is specifically within the contemplation of the invention that amounts different than those described above may be used to provide the desired thermal stability, depending on the particular application. For example, in one embodiment, a suitable system for increasing polymer stability may comprise 0.1% by weight to 99% by weight synthetic polymer and 0.1% by weight to 99% by weight TEA. More preferably, in one embodiment the system may comprise

0.3% by weight to 5% by weight synthetic polymer and 0.2% by weight to 20% TEA. Still more preferably, in one embodiment the system may comprise 0.6% by weight to 2.6% by weight synthetic polymer and 0.6% by weight to 11.1% by weight TEA.

[0041] Significantly, like PEG, TEA is miscible in water, which prevents any undesirable phase separation. While the foregoing embodiments reference a limited number of compounds, it should be recognized that chemical compounds having the same general characteristics also will function in an analogous fashion. For example, it is expressly within the scope of the present invention that methyldiethanol amine (MDEA), dimethylethanol amine (DMEA), diethanol amine (DEA), monoethanol amine (MEA), or other suitable tertiary, secondary, and primary amines and ammonia could be substituted, in whole or in part, for the triethanol amine described herein. In addition, it also is expressly within the scope of the invention that other mixed TEA systems may be used as additives, such as a TEA / glycol system or a TEA / alcohol system. Suitable alcohols would include methanol, ethanol, n-propanol and its isomers, n-butanol and its isomers, n-pentanol and its isomers, n-hexanol and its isomers, *etc.*

[0042] Similarly, other synthetic polymers may be substituted for PEG, such as, for example, poly(acrylonitrile), poly(acetates), and other synthetic polymers known in the art. We have additional data showing the utility of amines in non-CaBr₂-containing brine solutions, specifically including those based on NaHCO₂, KHCO₂, CsHCO₂, and combinations thereof. Furthermore, it should be noted that while most of the above examples discuss the utility of amines in CaBr₂-containing brine solutions, it will be clear to one of ordinary skill in the art that other brine solutions, such as ZnCl₂, CaBr₂, and ZnBr₂, NaCl, KCl, NH₄Cl, MgCl₂, seawater, NaBr, Na₂S₂O₃, and combinations thereof may be used.

[0043] In addition, while specific amounts of the chemicals used are described in the above embodiments, it is specifically within the contemplation of the invention that amounts different than those described above may be used to provide the desired thermal stability, depending on the particular application.

[0044] A proposed mechanism for how the addition of TEA assists in maintaining the stability of synthetic polymer systems is based on the belief that TEA may act as a pH buffer. Many of the above mentioned synthetic polymers contain ether linkages in the main chain of the polymer. There are mechanisms for the cleavage of ether linkages (which are slowly catalyzed by acidic conditions), which under severe conditions of stress, can be effected upon the backbone of bonds which tie the units of the polymer together. Cleaving one or more of the bonds which constitute the backbone of the polymer leads directly to de-polymerization and hence to degradation of the polymer. As stated above, some of these cleavage mechanisms are acid-catalyzed. Thus, by maintaining the pH level above that of the base brine pH, or as near to 7 as possible, TEA may help to prevent an acid-catalyzed degradation of a synthetic polymer.

[0045] In the above discussion involving an acid-catalyzed mechanisms for polymer degradation, it should be noted explicitly that both Bronsted-Lowry and Lewis definitions of acids are equally applicable. Thus in aqueous systems where acids may be present and acting as such through the Bronsted-Lowry definition of an acid, the role of the acid would be that of a "proton-donor" while the complementary role of the TEA would be that of a "proton-acceptor." Furthermore, in systems such as, for example, those containing the Lewis acid zinc bromide, where the acid may be acting as such through the Lewis definition of an acid, the role of the acid would be that of an "electron-acceptor" while the complementary role of the TEA would be that of a "electron-donor."

[0046] The present invention advantageously increases the effective temperature range for synthetic polymer systems in an inexpensive, easy-to-implement method. The addition of miscible amines into the synthetic polymer system dramatically increases the temperature resistivity of the solution and enhances the overall stability of the system. In addition, the present invention specifically contemplates that the above described compositions may be used to treat a well.

[0047] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.